CARNEGIE-MELLON UNIVERSITY
MELLON INSTITUTE

NASA Research Grant NGR-39-008-014

INVESTIGATION OF STRESS CORROSION CRACKING OF TITANIUM ALLOYS

Semi-Annual Progress Report No. 5

for the Period

June 1, 1968 through November 30, 1968

BY

E. G. Haney and W. R. Wearmouth

Carnegie-Mellon University
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213

(NASA-CR-100119) INVESTIGATION OF STRESS CORROSION CRACKING OF TITANIUM ALLOYS Semiannual Progress Report No. 5, 1 Jun. - 30 Nov. 1968 (Mellon Inst.) 29 p

N69-70416

Unclas
00/26 0198619

Gew 2/14/69

Approved Date

CARNEGIE-MELLON UNIVERSITY
MELLON INSTITUTE

NASA Research Grant NGR-39-008-014

INVESTIGATION OF STRESS CORROSION CRACKING OF TITANIUM ALLOYS

Semi-Annual Progress Report No. 5

for the Period

June 1, 1968 through November 30, 1968

BY

E. G. Haney and W. R. Wearmouth

Carnegie-Mellon University
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213

ABSTRACT

The cracking of 99.5 Ti, Ti-6Al-4V and Ti-13V-11Cr-3Al in methanolic solutions containing 0.01N HCl is shown to be a thermally activated process possessing activation energies of 9.21, 4.80 and 6.31 kcal/mole, respectively.

Methanolic solutions containing 10^{-5}N HCl readily produce failure in 99.5 Ti, Ti-6Al-4V and Ti-13V-11Cr-3Al, whereas in similar solutions containing 10^{-6}N HCl no failures are recorded after 2500 hours. Similarly, in "pure" methanol containing no chloride additions, no failures are recorded after 3000 hours. Electrode potential values show the similarity in behaviour between "pure" methanol and methanol containing 10^{-6}N HCl.

INTRODUCTION

The progress of the last 6 months is summarized in this report. The earlier work reported in Semi-Annual Progress Reports 1-4[1] was primarily concerned with the stress corrosion cracking of the titanium alloys: 99.0 Ti (foil), Ti-0.2 Pd (foil), Ti-5Al-5Sn-5Zr (foil), Ti-6Al-4V (foil and rod), and Ti-13V-11Cr-3Al (foil). The solutions employed were principally methanol containing HCl or NaCl and varying amounts of added water. Investigations of additions to methanol-HCl or -NaCl solutions other than water included: di-methyl sulphoxide, acetonitrile, acetic acid, acetone, methyl-ethyl-ketone, carbon tetrachloride, or the alcohols, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, n-octyl. It was shown that methanolic solutions containing only 10^{-4}N NaCl, a few parts per million, would readily crack 99.0Ti and Ti-6Al-4V. The effect of solution temperature was studied for Ti-13V-11Cr-3Al in CH_3OH-0.01N HCl.

Research in the subsequent period has extended the work on the effect of temperature to 99.5Ti and Ti-6Al-4V. Also a detailed study has been made of the effect of chloride concentration on the cracking of 99.5Ti, Ti-6Al-4V, and Ti-13V-11Cr-3Al, in CH_3OH-H_2O-HCl solutions[2].

MATERIALS AND PROCEDURES

The mill compositions of all the alloys investigated in the latest period are given in Table I. The tensile properties are presented in Table II. All the alloys were received as foil (~ 0.003" thick), having been rolled on a Sendzimir mill and sheared to 1/4" wide strips cut parallel with the rolling direction by automatic equipment at the mill. Heat treatment was accomplished in an electric resistance furnace after first sealing the specimens in vycor tubing under a partial pressure of helium.

The details of equipment, apparatus, chemicals and testing procedures were reviewed in detail in Semi-Annual Progress Report 4.

EXPERIMENTAL RESULTS

The continued work investigating the effect of temperature on the time to failure is shown in Figure I for 99.5 Ti and Ti-6Al-4V in CH_3OH-0.01N HCl as a function of water content. Like the results obtained previously for Ti-13V-11Cr-3Al it is seen that for any particular temperature a minimum time to failure is found. On plotting the shortest time to failure for each temperature against the reciprocal of the absolute temperature, a straight line is obtained. Figure 2 shows these linear plots, including that for Ti-13V-11Cr-3Al for comparison. From the usual Arrhenius treatment of such data, activation energies were calculated for each of the alloys, which are also recorded on Figure 2.

Figures 3 and 4 show the behaviour with and without applied stress of 99.5 Ti in CH_3OH-0.01N HCl solutions, as a function of heat treatment. It is evident that annealing the cold worked structure increases its susceptibility to failure under stress and also decreases its corrosion resistance. Figure 5 shows similar corrosion curves for 99.5 Ti, Ti-6Al-4V and Ti-13V-11Cr-3Al in CH_3OH-0.01N HCl containing 0.09% H_2O. The Ti-6Al-4V foil is shown to be superior in its resistance to this form of attack. The corresponding time to failure curves for Ti-13V-11Cr-3Al alloy and Ti-6Al-4V alloy in methanolic solutions containing 0.01N HCl are shown in Figures 6 and 8, respectively, as a function of water content.

The effect of chloride ion concentration in methanol-water solutions on the failure times is shown in Figs. 7, 8 and 9 for 99.5Ti, Ti-6Al-4V and Ti-13V-11Cr-3Al, respectively. Each curve shows a typical minimum with failure times first decreasing and then increasing sharply with increasing amounts of water. The alloys were readily cracked with only 10^{-5}N HCl present (third part per million), but much less water was required to inhibit the cracking as compared with specimens exposed to solutions containing 10^{-2}N HCl. There was approximately an order of magnitude increase in the time to failure at the minimum accompanying a three-order of magnitude change in chloride content from 10^{-2}N to 10^{-5}N HCl. Dropping the chloride content another order of magnitude to 10^{-6}N HCl has produced no failures for the 99.5Ti and Ti-6Al-4V after 3000 hours and 1500 hours, respectively, i.e., more than an order of magnitude beyond the failure times at the minimum for specimens exposed to solutions containing 10^{-5}N HCl. The Ti-13V-11Cr-3Al alloy foils exposed to solutions containing 10^{-6}N HCl always broke in contact with the polyethylene bottle and such results were discounted because experience had indicated that contact breaks generally occurred at shorter times to failure than normal breaks at equivalent quantities of water and chloride.

Figures 10 and 11 show the values of electrode potential after one hour, for 99.5Ti and Ti-13V-11Cr-3Al in methanol-water solution compositions containing various quantities of HCl. The curves for solutions containing 10^{-2}N HCl and 10^{-5}N HCl are characteristic of those observed for titanium alloys that crack in methanol-water-HCl environments, i.e., low values of electrode potential at the lowest water concentrations followed by a sharp increase to more noble values as water is added and finally a levelling off with additional water. However, the two electrode potential curves for solutions containing 10^{-6}N HCl and no added HCl are characterized by no sharp changes in slope except at much higher water concentrations. With less than 0.25% water, the electrode potential values are more noble the lower the chloride concentrations.

Table III shows the results of corrosion without applied stress on the tensile properties of single specimens of 99.0Ti, in the cold-rolled and cold-rolled and annealed states, for extended periods of time. The solution employed was methanol containing 0.02% water with no added chlorides. It can be seen that for periods of time up to approximately 4500 hours no deterioration has resulted in the tensile properties.

DISCUSSION

The effect of varying the solution temperature within the range -45°C to +50°C provides some interesting results. The failure times, as expected, are found to be increased at the lower temperatures, but also the minimum in the curves occurs over a more restricted range of water contents as the temperature is decreased, without much shift in position with respect to water. It is, therefore, apparent that the conditions which promote the formation of the minimum operate throughout the temperature range investigated. Assuming the validity of plotting the minimum time to failure versus the reciprocal of the absolute temperature, the linearity of the Arrhenius type plots suggests a thermally activated process possessing a characteristic activation energy, which is not too different for the three alloys. Although the values of the activation energies are similar to those for the diffusion of hydrogen in α and β titanium (12.38 $\pm$ 0.68 and 6.64 $\pm$ 0.50 kcal/mole respectively[(3)]), it is felt that there is not a sufficient correspondence for a direct comparison to be made. However, from the results of Mori, et al.[(4)], who tested U-bend specimens of sheet titanium, 0.04" thick, in methanol - 0.4% HCl at varying temperatures, an activation energy of approximately 10.2 kcal/mole can be calculated for the range 10°C to 50°C which is very close to the value obtained in the present work. Also, Menzies and Averill[(5)] have studied the anodic behaviour of titanium in methanol-HCl solutions; in particular they determined corrosion currents for titanium in methanol-2N HCl as a function of temperature. On plotting these results on an Arrhenius plot, an activation energy of 10.9 kcal/mole can be calculated. There is, therefore, a close correspondence between this value and that determined in the present work for stressed specimens, which is indicative of the important part played in the failure process by anodic dissolution.

The time to failure curves, plotted as a function of water content for 99.5Ti, Ti-6Al-4V and Ti-13V-11Cr-3Al are typical of those obtained previously[(1)]; as the water content is increased, the times to failure pass through a minimum until enough water is added to inhibit the cracking process. The one-hour electrode potential curves for solutions containing 0.01N HCl or 0.01N NaCl are also characteristic of those observed previously for titanium alloys that crack in methanol-water-HCl environments, i.e., low values of electrode potential at the lowest water concentrations followed by a sharp increase to more noble values as water is added and finally a levelling off with additional water (see later).

In 99.5Ti, the effect of annealing the cold worked structure results in an equiaxed grain structure which markedly increases its susceptibility to failure. Apparently the increased susceptibility is due to the presence of the grain boundaries, as the crack path is wholly intergranular. However, although the times to failure are different by an order of magnitude, the electrode potential curves are not too different. Thus, although the absolute values of electrode potential give some indication as to whether or not failure might be expected, they do not indicate the relative susceptibilities to failure.

All three alloys are attacked in the absence of stress, as illustrated in Figures 4 and 5. The effect of annealing the cold worked 99.5Ti produces a substantial decrease in its resistance to deterioration by methanolic solutions, thus supporting the important effect of corrosion mechanisms in the cracking process. Alloy Ti-6Al-4V shows the greatest resistance to the type of attack, Figure 5. However, on comparing the times to failure for e.g., 99.5Ti and Ti-6Al-4V in CH_3OH-0.01N HCl - 0.09% H_2O, viz., 3.6 hours and 5.5 hours, respectively, with the free corrosion curves, it is seen that factors other than corrosion effects must be operative in the cracking mechanism.

As can be seen from Figures 10 and 11, the electrode potential curves for methanolic solutions containing 10^{-2}N HCl and 10^{-5}N HCl are characteristic of those observed for titanium alloys. However, the two curves for solutions containing 10^{-6}N HCl and no added HCl are characterized by no sharp changes in slope except at much higher water contents. With less than 0.25% water, the electrode potential values are more noble the lower the chloride concentrations. Generally, therefore, the values of electrode potential give a very strong indication as to whether or not failure will occur, i.e., whether or not the potential of the specimen surface is in the critical range for crack initiation. The inability of "pure" methanol to crack titanium receives support from corrosion results (Table III) where no deterioration in tensile properties of 99.0Ti is found up to 4000 hours. If there is a limit to the amount of chloride needed to crack the alloys investigated, then it would be definitely less than 1/3 ppm (10^{-5}N HCl). The data for time to failure of 99.5Ti and Ti-6Al-4V suggest that the limit probably occurs between 10^{-5} and 10^{-6}N HCl.

CONCLUSIONS

1) The cracking of 99.5Ti, Ti-6Al-4V and Ti-13V-11Cr-3Al in methanolic solutions containing 0.01N HCl is shown to be a thermally activated process, possessing activation energies of 9.21, 4.80 and 6.31 kcal/mole, respectively.
2) Annealing cold rolled specimens of 99.5Ti reduces the time to failure by an order of magnitude while requiring more water for inhibiting the cracking process.

3) No deterioration in tensile properties is produced in 99.0Ti in "pure" methanol for times up to 4000 hours.

4) Methanolic solutions containing 1/3 ppm chlorides (10^{-5}N HCl) are capable of cracking 99.5Ti, Ti-6Al-4V and Ti-13V-11Cr-3Al, whereas similar solutions containing 10^{-6}N HCl produce no failures in the times investigated.

Elwood G. Haney
ELWOOD G. HANEY
Fellow

EGH:sa
R: 2/10/69
T: 2/11/69

FUTURE WORK

1) An investigation into the behaviour of titanium in methanolic solutions containing varying concentrations of NaBr and NaI, with respect to times to failure and electrode potentials was recently started. This will be complementary to the work presently reported on the effect of varying concentrations of chloride.

2) A detailed study will be made of the effects of applied anodic and cathodic currents on stressed specimens of Ti-6Al-4V in methanolic solutions, varying such solution parameters as chloride concentration and water content.

3) Rod tensile specimens of Ti-6Al-4V and Ti-5Al-5Sn-5Zr, having an 0.125" diameter gauge length, will be tested, primarily to make a fractographic examination of the fracture surface after failure in the methanol-water-chloride solutions.

4) The degree of purity of the methanol will be altered by using different grades and any resulting variation in the failure times of stressed specimens will be investigated in terms of the impurity content of the methanol.

REFERENCES

1. E. G. Haney, et al., Progress Report Nos. 1, 2, 3, 4, NASA Research Grant NGR-39-008-014.

2. E. G. Haney and W. R. Wearmouth, Corrosion (in press).

3. R. J. Wasilewski and G. L. Kehl, Metallurgia, Manchr., Vol. 50, 225 (1954).

4. K. Mori, A. Takamura and T. Shimose, Corrosion, Vol. 22, 29 (1966).

5. I. A. Menzies and A. F. Averill, Electrochemica Acta., Vol. 13, 807 (1968).

TABLE I

Chemical Composition, Weight Percent

Alloy	Designation	Al	V	Cr	Fe	O	C	N	H
99.5Ti	Ti-35A				.07	.07	.023	.010	.004
99.0Ti	Ti-75A				*	*	*	*	*
6Al-4V	Ti-6Al-4V	6.4	4.0		.08		.02	.008	.013
13V-11Cr-3Al	Ti-13V-11Cr-3Al	3.2	13.8	10.6	.21	.12	.04	.030	.013

* Not available.

TABLE II

Tensile Properties of Titanium Alloys

Alloy	Condition	0.2% Offset Yield Strength (KSI)	Ultimate Tensile Strength (KSI)	Elongation % in 4"
99.5Ti	C.R.*	103.6	127.2	6.9
99.5Ti	Annealed 1 hr. at 1300°F	34.9	47.7	28.8 (in 2")
99.0Ti	C.R.*	129.3	142.2	7.2
99.0Ti	Annealed 2 hr. at 1025°F	74.5	90.8	29.9
6Al-4V	C.R.* and A†	116.3	148.9	9.1
13V-11Cr-3Al	C.R.* and A†	134.6	135.1	25.9

* Cold rolled

† Annealed

TABLE III

Tensile Properties of 99.0Ti after Exposure to "Pure" Methanol with no Applied Load

Cold Rolled Foil

Time in Solution, Hr.	Elongation % in 2"	Ultimate Tensile Strength KSI
0	7.2	138.6
260	7.0	141.5
402	6.5	139.0
1000	7.5	140.2
4536	6.3	139.0
Foil, Cold Rolled and Annealed 2 hrs. at 1025°F		
0	30.4	90.8
402	31.0	86.1
1000	37.0	84.9
2100	31.5	84.9
3070	33.0	81.2
4200	29.2	88.6

BASIC DISTRIBUTION LIST 32

Herbert F. Hardrath
SRD-Fatigue Branch
Mail Stop 129
Langley Research Center
Hampton, Virginia 23365

Eldon E. Mathauser
SRD-Structural Materials Branch
Mail Stop 188A
Langley Research Center
Hampton, Virginia 23365

G. Mervin Ault
Mat. Process Lab.
Mail Stop 105-
Lewis Research Center
Cleveland, Ohio 44135

Albert E. Anglin, Jr.
Airbreathing Engines Division
Mail Stop 54-
Lewis Research Center
Cleveland, Ohio 44135

Robert E. Johnson
SMD Experimental Mech.
Code ES4
Manned Spacecraft Center
Houston, Texas 77058

Wilbur A. Riehl
Code R-P&VE-MC
Building 4612
Marshall Space Flight Center
Huntsville, Alabama

Charles A Hermach
Materials Research
Mail Stop 240-1
Ames Research Center
Moffett Field, California

Naval Research Laboratory
Code 2300
Washington, D.C.
ATTN: Dr. B. F. Brown

U.S. Navy Marine Engineering Laboratory
Alloys Division
Annapolis, Maryland 21402
ATTN: Mr. W. L. Williams

Dr. Robert I. Jaffee
Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201

Mr. Harold H. Block
Consulting Metallurgist
7120 W. 90th Street
Los Angeles, California 90045

Mr. Elihu F. Bradley
Chief, Materials Engineering
Pratt & Whitney Aircraft
East Hartford, Connecticut

Professor Mars G. Fontana
Chairman, Dept. of Metallurgical
Engineering
Ohio State University
Columbus, Ohio

Mr. Dean Hanink
Manager, Materials Laboratory
General Motors Corp.
Allison Division
Tibbs Avenue
Indianapolis, Indiana 46206

Mr. Louis P. Jahnke
Manager of Metallurgy
General Electric Corp.
Flight Propulsion Division
Cincinnati, Ohio 45215

Mr. John V. Long
Director of Research
Solar Corp.
2200 Pacific Highway
San Diego, California

Dr. Alan M. Lovelace
Chief Scientist
Air Force Materials Laboratory
Wright-Patterson AFB, Ohio 45433

Mr. Ward Minkler
Manager of Technical Service
Titanium Metals Corp. of America
233 Broadway
New York, New York 10007

Mr. Winston H. Sharp
Connecticut Metallurgical Corp.
2 State Street
Hartford, Connecticut 06103

Carnegie-Mellon University
Mellon Institute
4400 Fifth Ave.
Pittsburgh, Pennsylvania 15213
ATTN: Dr. H. L. Anthony

Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201
ATTN: Mr. Walter Boyd

Titanium Metals Corp. of America
Henderson, Nevada
ATTN: Mr. H. W. Rosenberg

Reactive Metals, Inc.
Niles, Ohio
ATTN: Mr. H. B. Bomberger

Crucible Steel Co. of America
P. O. Box 7257
Pittsburgh, Pennsylvania 15213

Savannah River Laboratory
Nuclear Materials Division
E.I. duPont deNemours Co.
Aiken, South Carolina
ATTN: Mr. S. P. Rideout

National Bureau of Standards
Metallurgy Division
Washington, D.C.
ATTN: Mr. Hugh Logan

Materials Research Laboratory
22333 Governors Highway
Richton Park, Illinois

Ohio State University Research Foundation
Ohio State University
Columbus, Ohio
ATTN: Professor Franklin Beck

Douglas Aircraft Company
Newport Beach, California
ATTN: Dr. N. A. Tiner

Lockheed-California Company
Box 551
Burbank, California
ATTN: Mr. George Wald

Douglas Aircraft
Aircraft Division
Long Beach, California
ATTN: Mr. R. A. Simpson

The Boeing Company
Aerospace Group
P. O. Box 3707
Seattle, Washington 98124
ATTN: Dr. T. R. Beck

SUPPLEMENTARY DISTRIBUTION LIST

Dr. James W. Savage
Senior Metallurgist
Science Center/Aerospace and System Group
North American Rockwell Corp.
1049 Camino Dos Rios
Thousand Oaks, California 91360

Bernard Wendrow
North American Rockwell Corp.
Building 305, Mail code GA19
12214 Lakewood Blvd.
Downing, California 90241

Dr Hugh R. Gray
Mail Stop 49-1
NASA
Lewis Research Center
2100 Brookpark Rd.
Cleveland, Ohio 4135

Hercules, Inc.
P. O. Box 98
Bacchus Works Technical Library
Magna, Utah

Research Institute for Advanced Studies
Materials Science Dept.
1450 South Rolling Road
Baltimore, Maryland 21227
ATTN: Dr. A. J. Sedriks

Mr. A. H. Freedman
Northrop Norair
Dept. 3771-60
3901 West Broadway
Hawthorne, California

Professor H. W. Paxton
Head, Department of Metallurgy and Materials
Science
Carnegie-Mellon University
Doherty Hall
Schenley Park
Pittsburgh, Pennsylvania 15213

Dr. J. B. Arots
Research Center
Hercules, Inc.
Wilmington, Delaware 19899

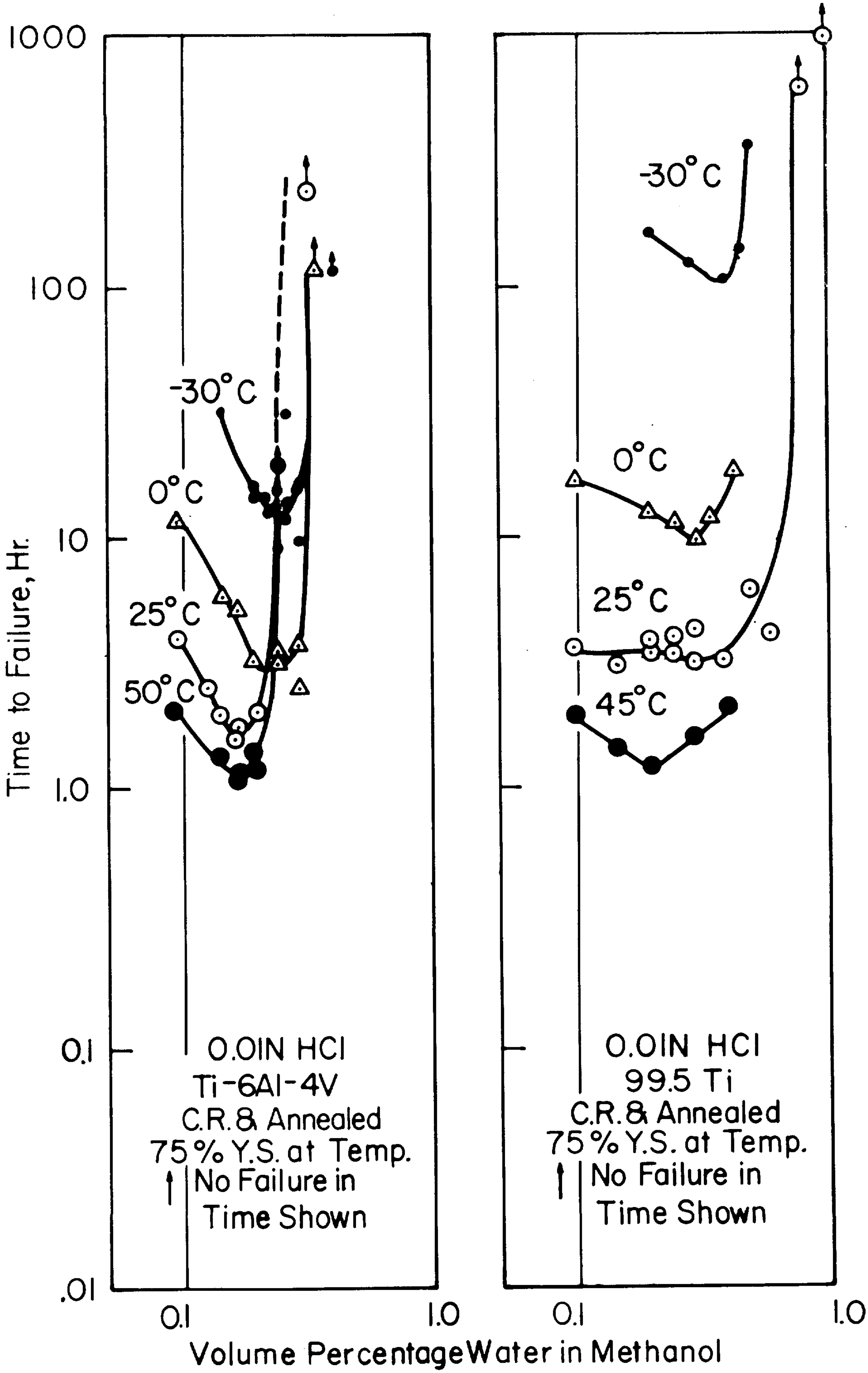

FIGURE 1. Effect of temperature on time to failure

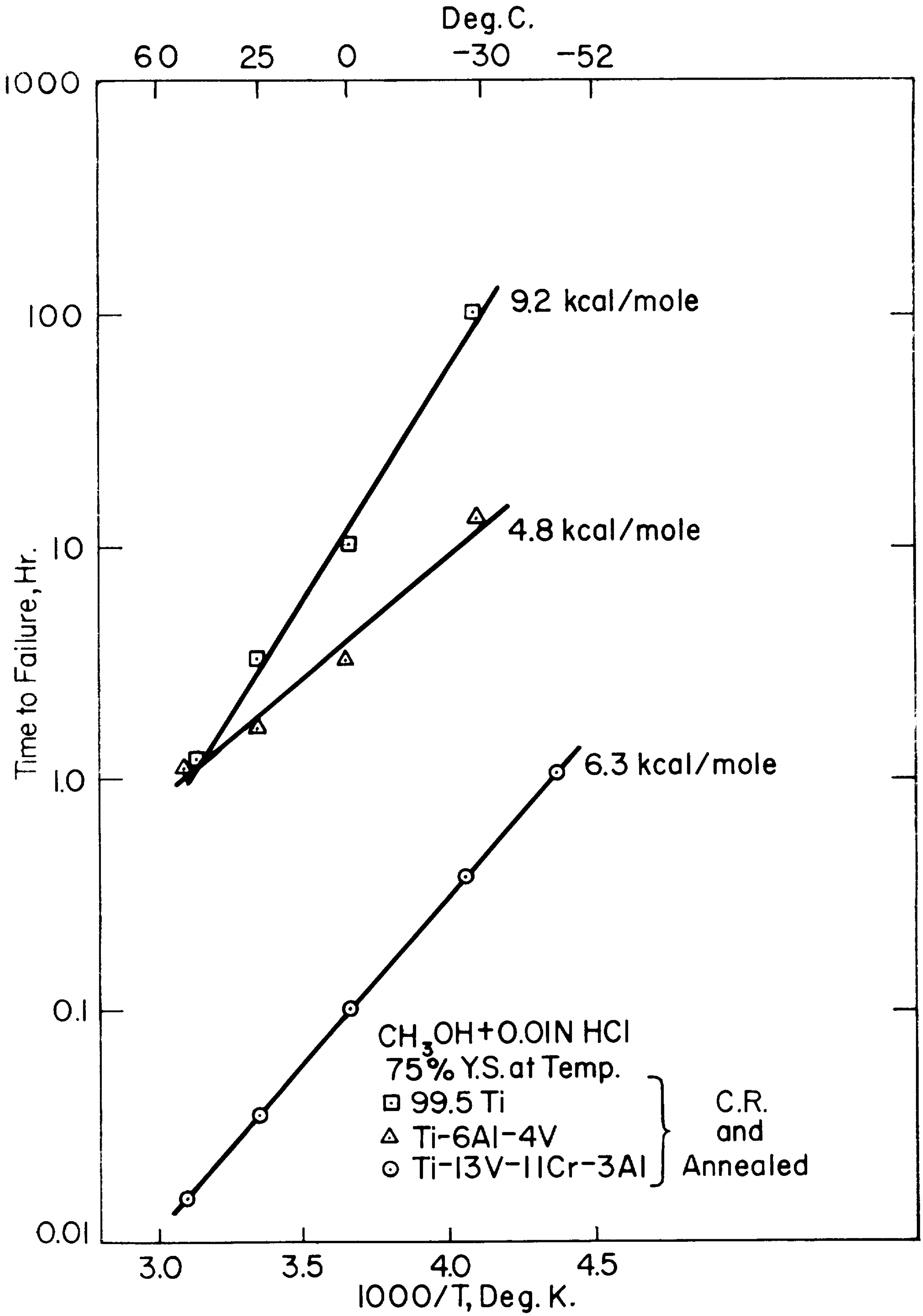

FIGURE 2. Effect of reciprocal temperature on minimum time to failure.

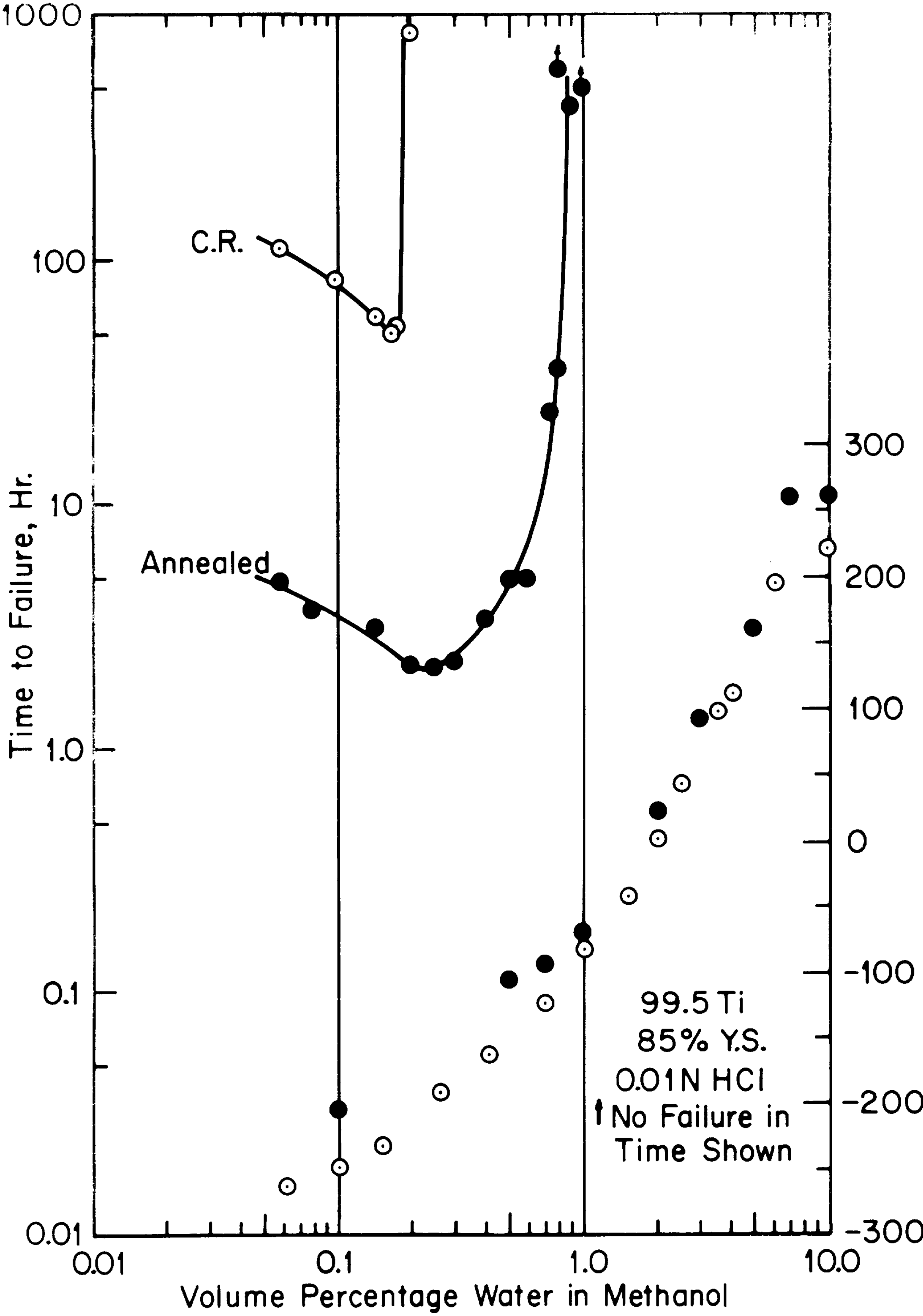

FIGURE 3. Comparison of time to failure with one-hour electrode potential values.

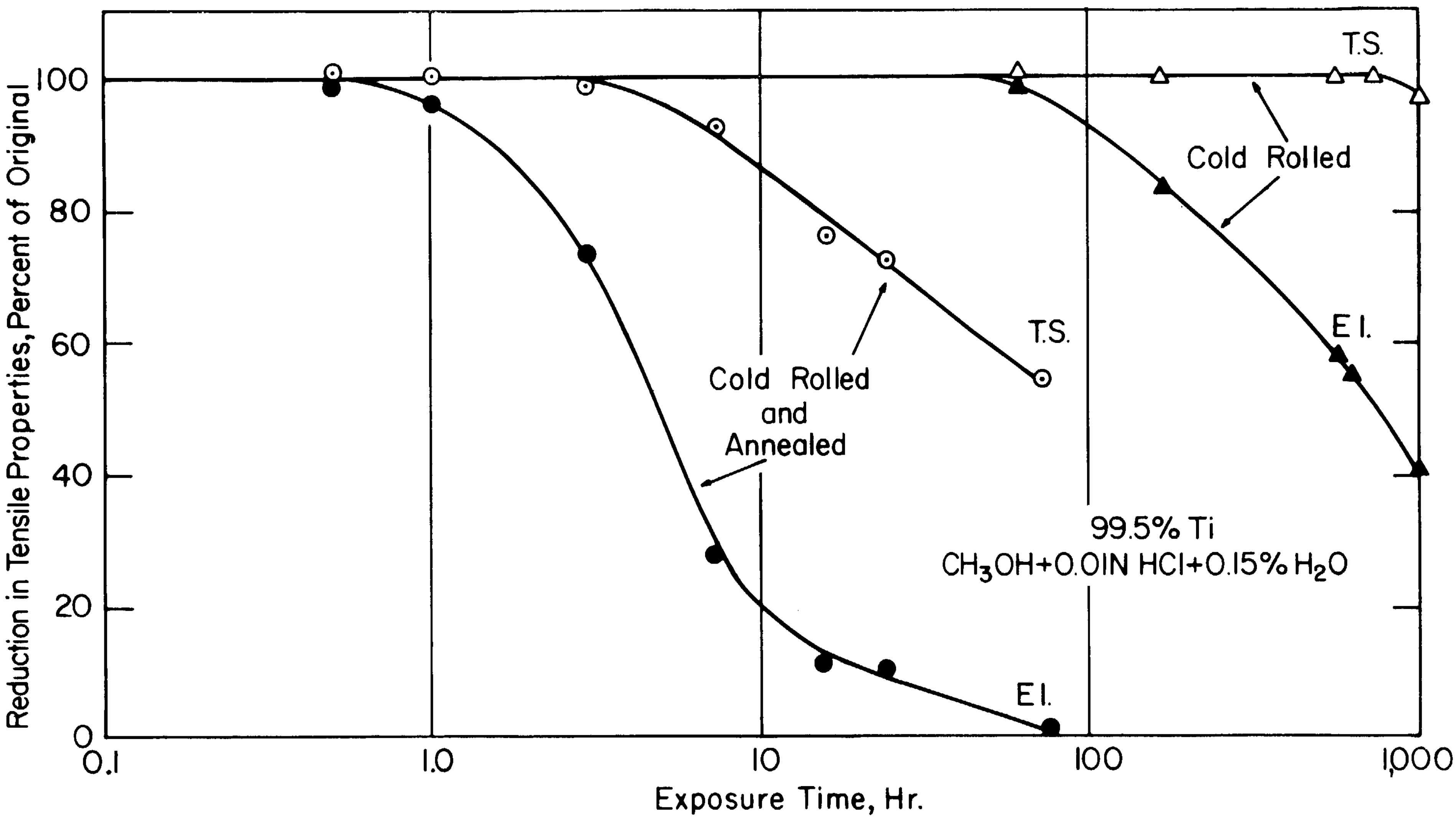

FIGURE 4. Deterioration in tensile properties after exposure to solution with no applied load.

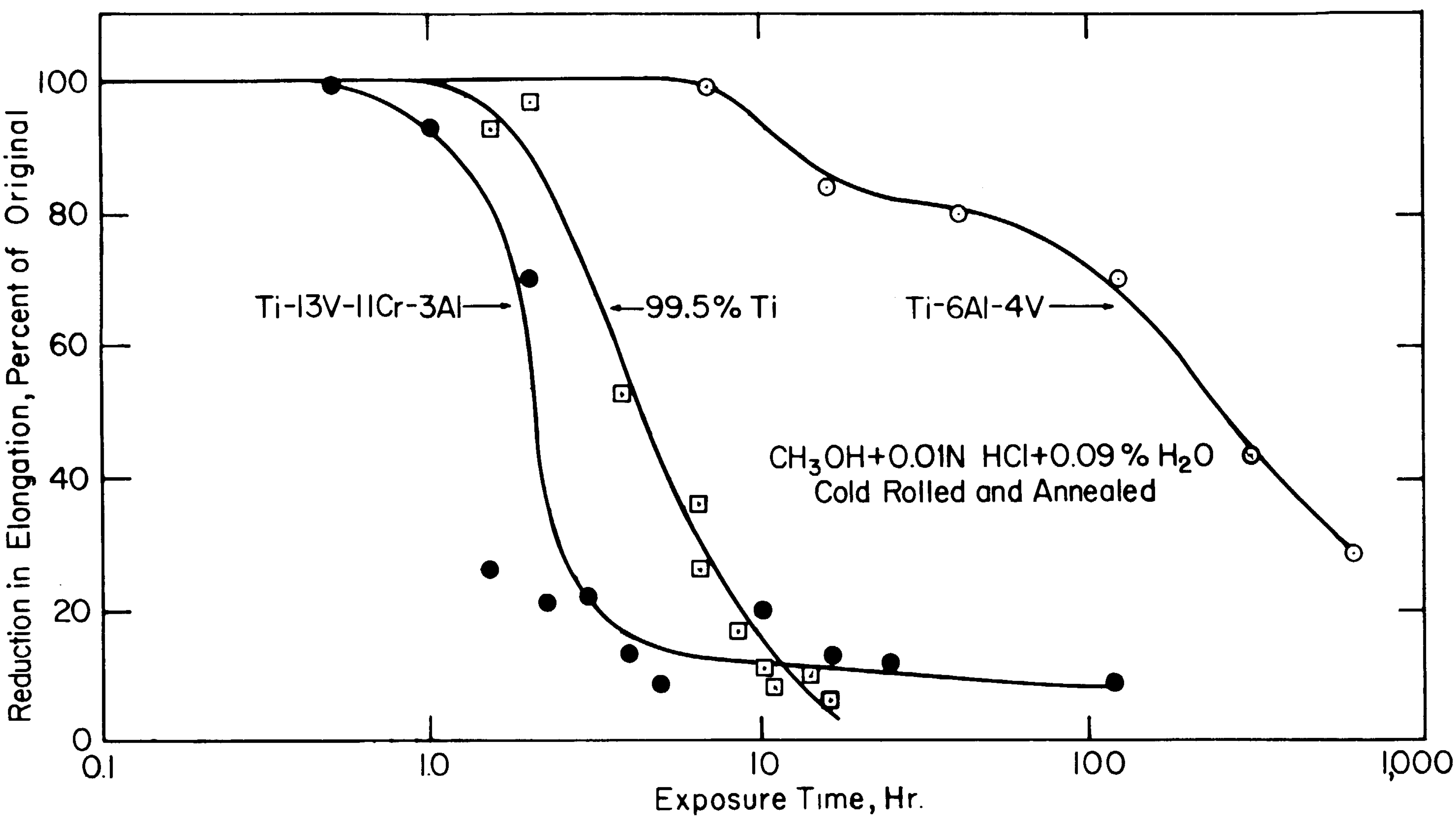

FIGURE 5. Deterioration in tensile properties after exposure to solution with no applied load.

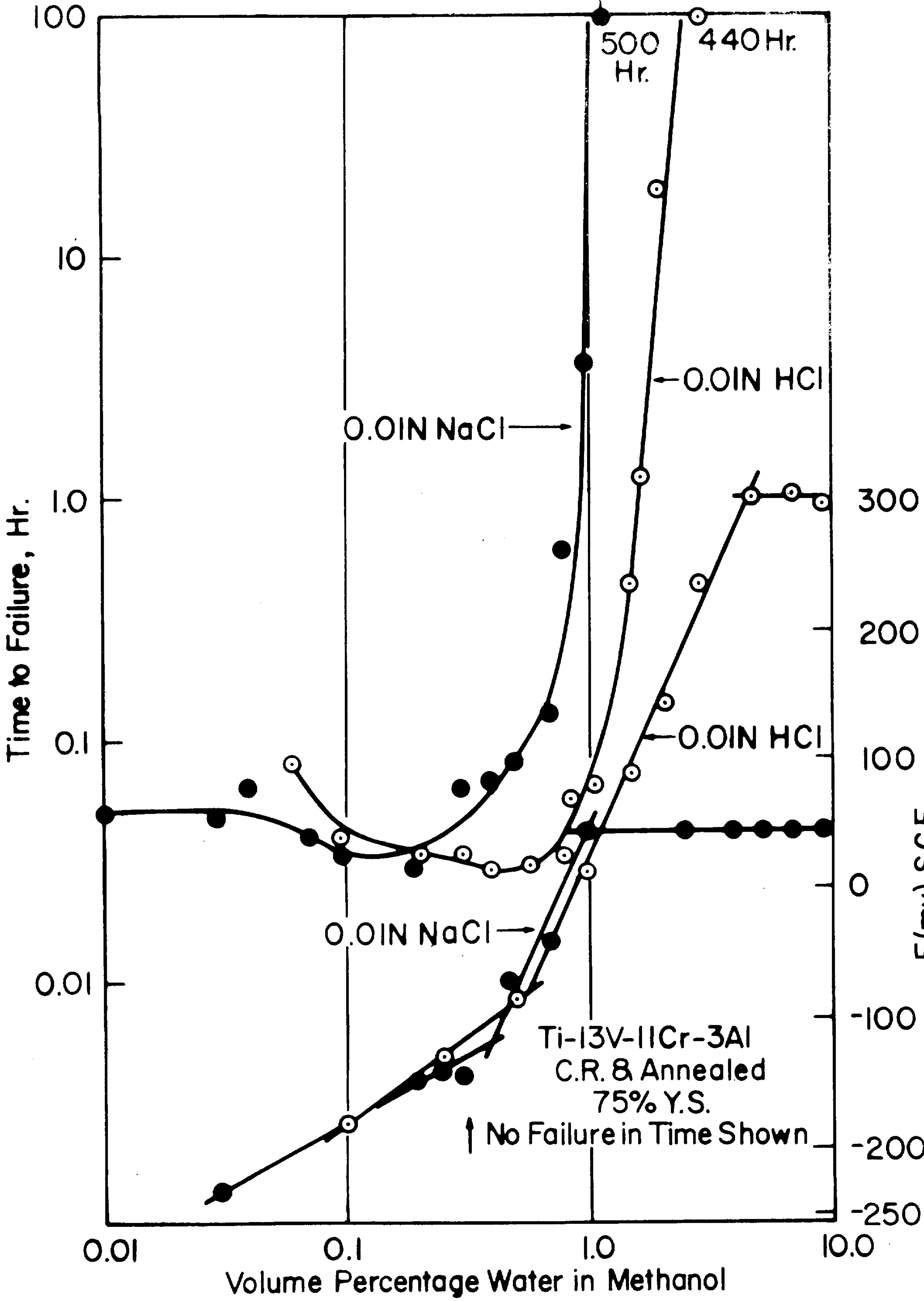

FIGURE 6. Comparison of time to failure with one-hour electrode potential values.

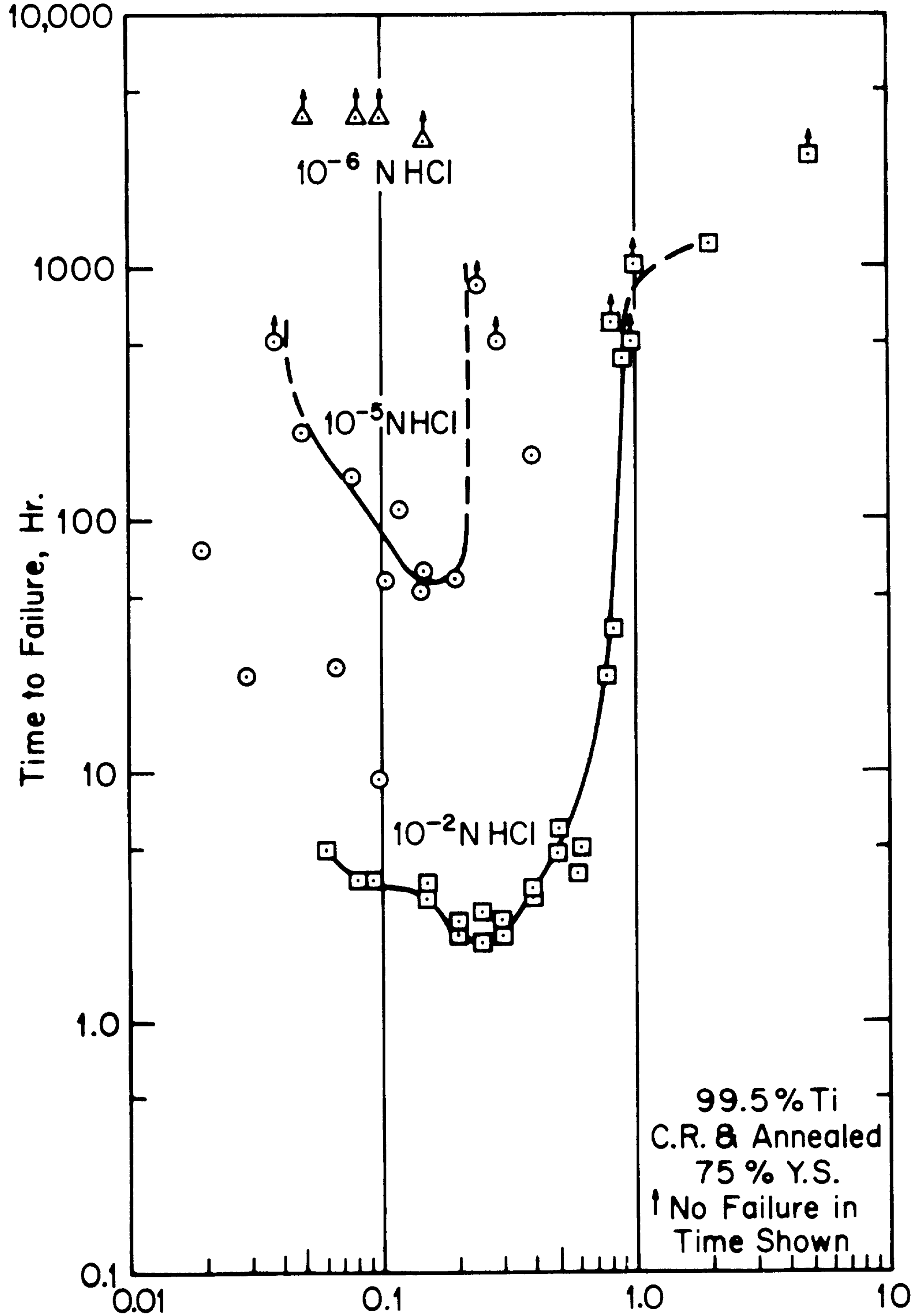

FIGURE 7. Effect of HCl and water content on time to failure.

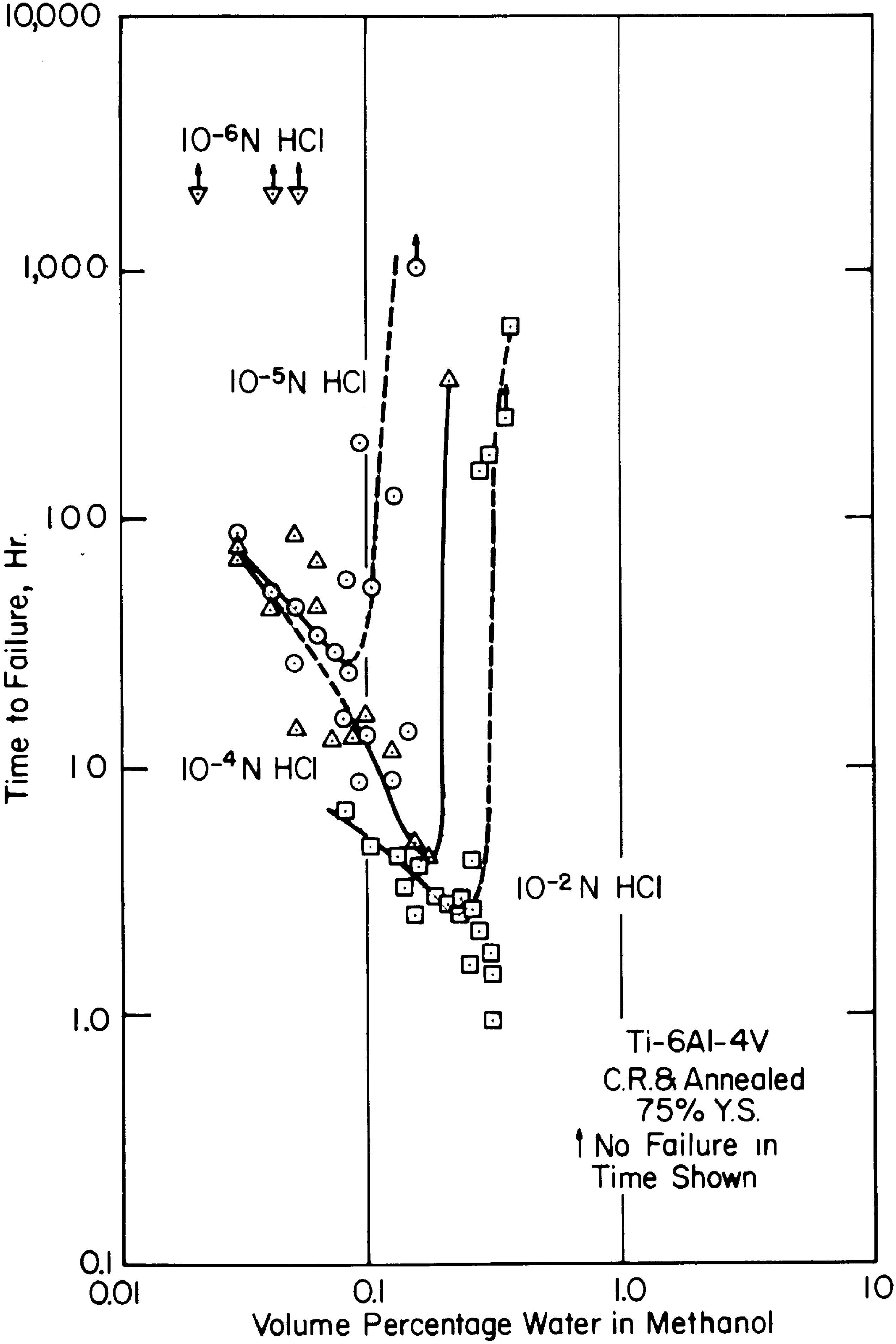

FIGURE 8. Effect of HCl and water content on time to failure.

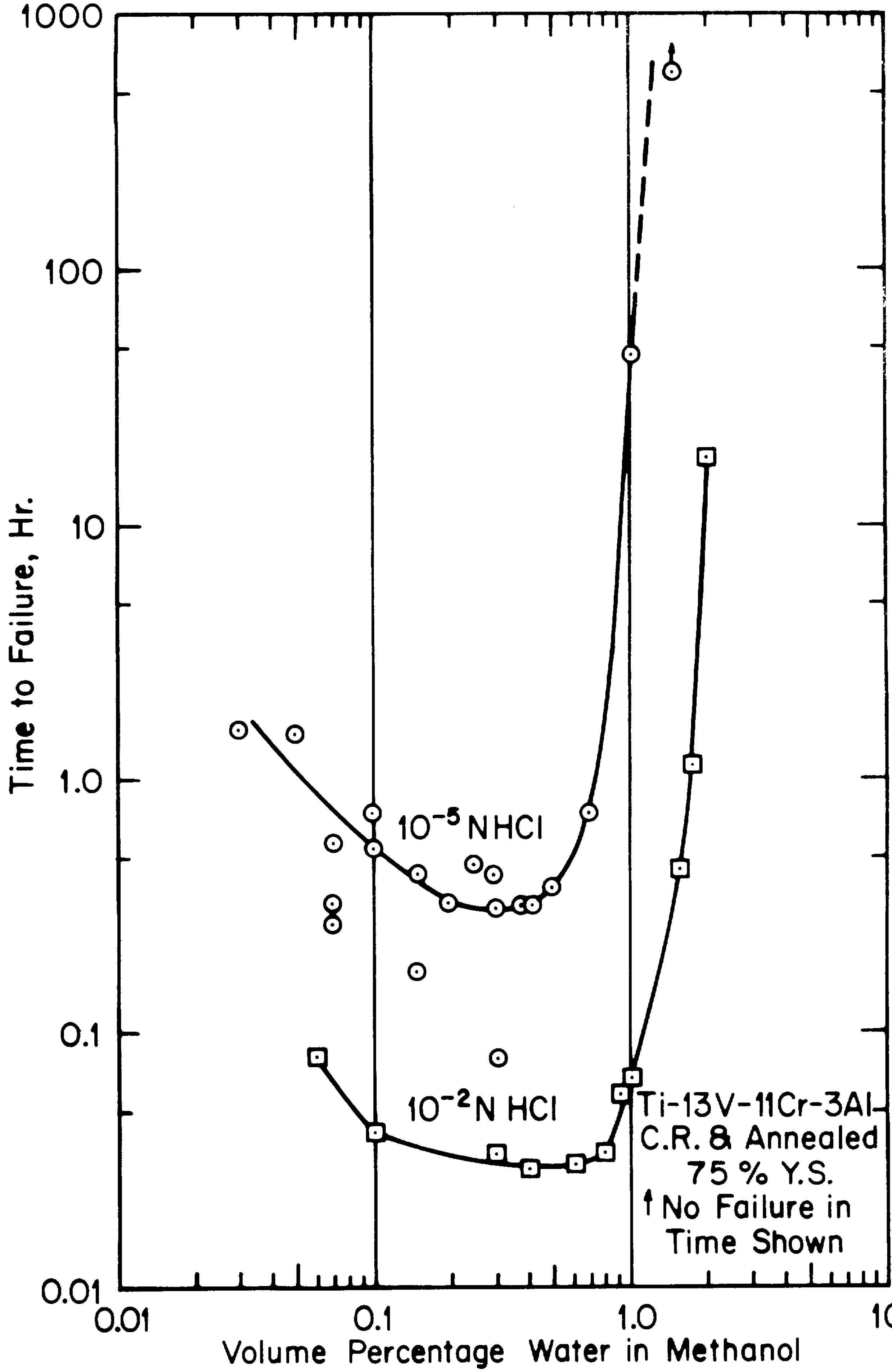

FIGURE 9. Effect of HCl and water content on time to failure.

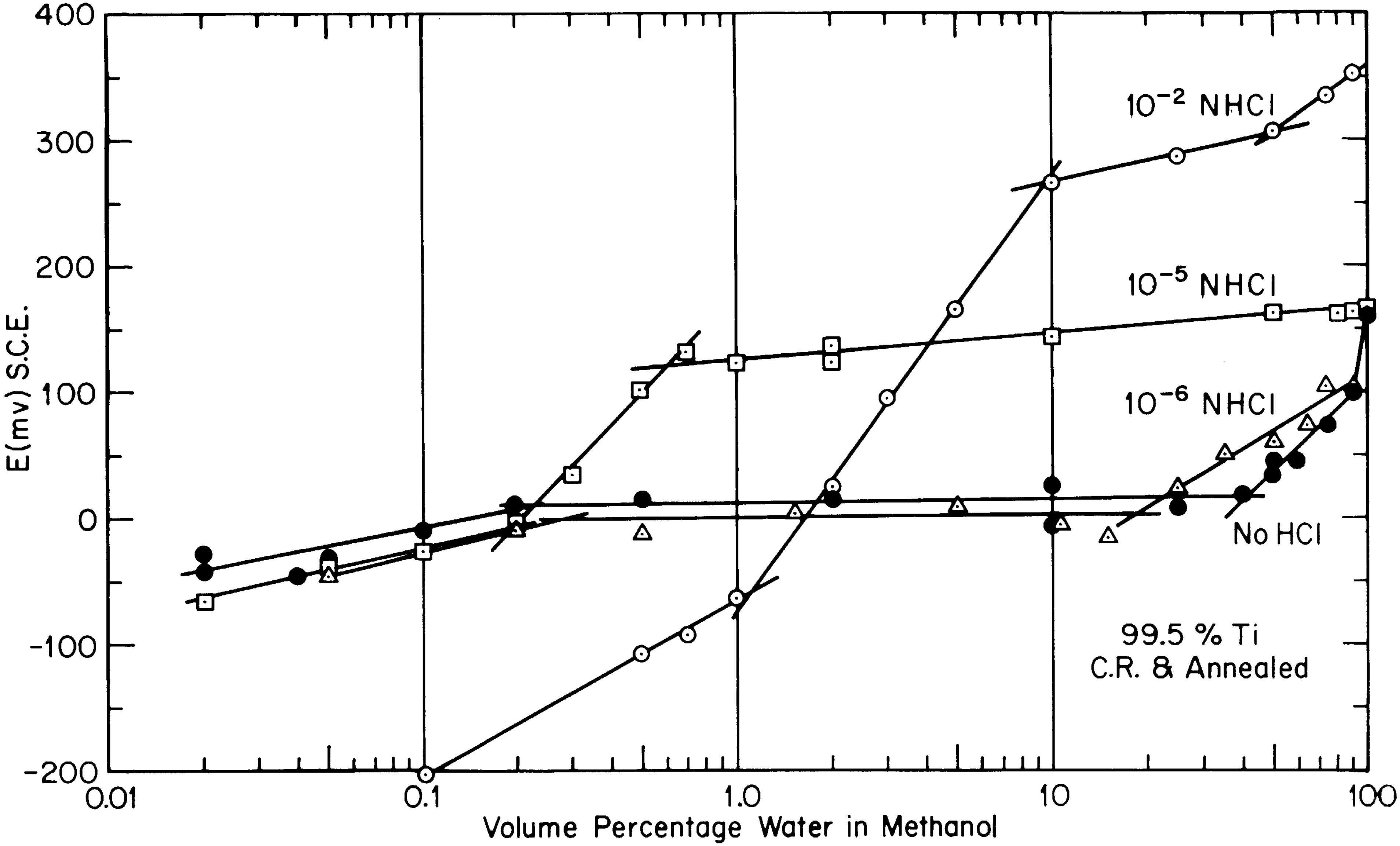

FIGURE 10. One hour electrode potential values as a function of HCl and water content.

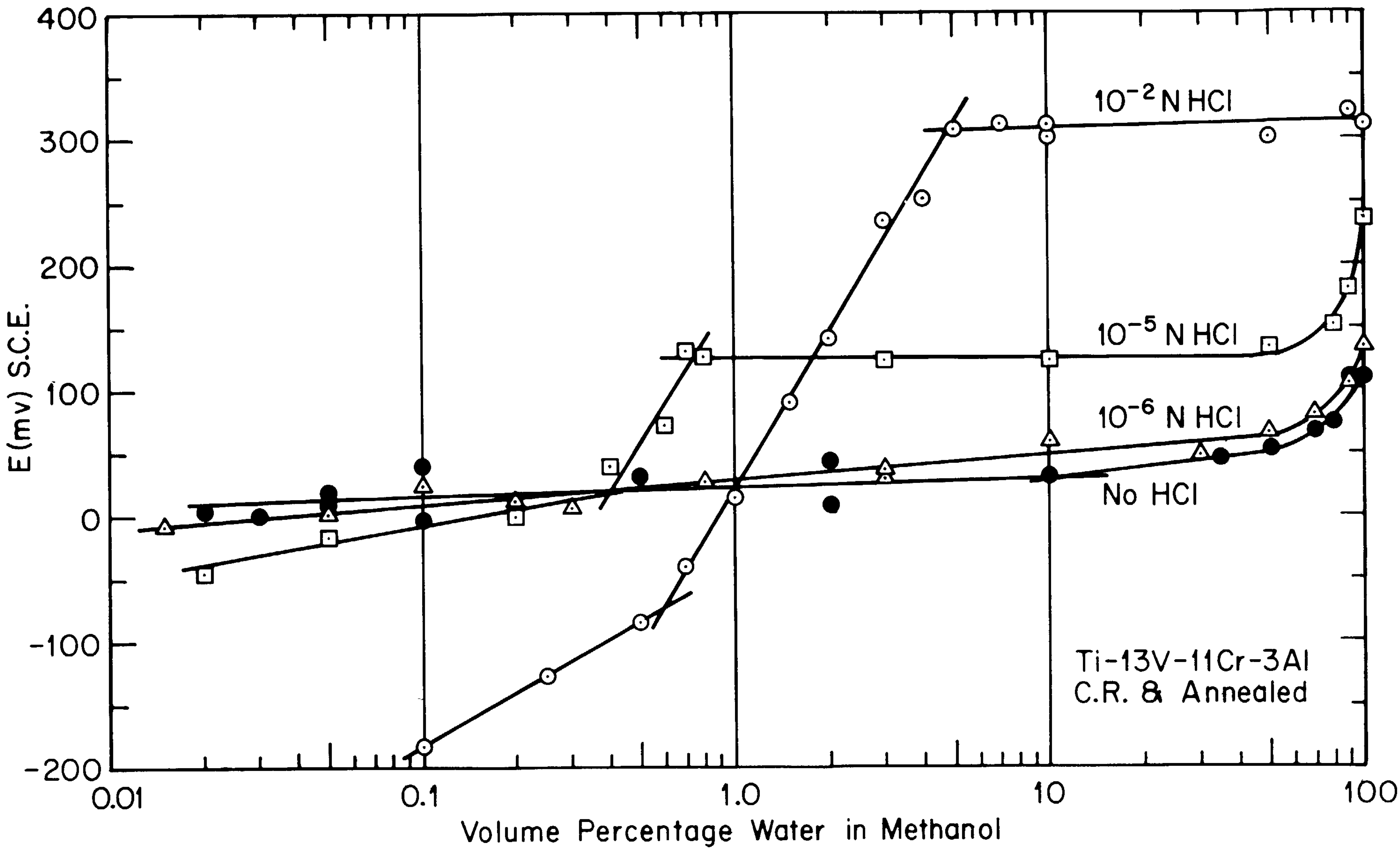

FIGURE 11. One hour electrode potential values as a function of HCl and water content.